Hollinger Corp.
pH 8.5

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THE USE OF THE CALORIMETER IN DETECTING ADULTERATIONS OF BUTTER AND LARD.[1]

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WHILE engaged in a study of the comparative value of butters and oleomargarines, it occurred to one of us that possibly the determinations of their respective heats of combustion might be useful if taken in connection with other data. Prof. Atwater, who has for some time been conducting experiments with an improved calorimeter, very kindly consented to burn such samples as might be sent to him. The first results were so interesting that it occurred to us at once that this method might be useful in detecting the adulteration of butter with oleomargarine, and also perhaps in distinguishing between lards of different sources and compound lards. Accordingly, some specially selected samples of which duplicates were kept in our laboratory, were sent to Prof. Atwater, and in the case of the butters and oleomargarines the results confirmed our first suppositions. In the use of the lards, however, the results were not so sharply distinctive, but taken in conjunction with other analytical data will prove, as we will endeavor to show,

[1] Read at the Cleveland meeting, Dec. 31, 1895.

TABLE I.

Analyses of Butters and Oleomargarines.

No.	Manufacturer.	Specific gravity at 100° C.	Water. per cent.	Vol. $\frac{n}{10}$ $Ba(OH)_2$ for 2.5 grams.	Salt. per cent.	Casein. per cent.	Ash. per cent.	Melting point. °C.	Iodine equivalent.	Combustion calories per gram. Atwater.	Cottonseed-oil, Bechi's test.	Coloring matter.	Sample No.
1	Oakdale M'f'g Co., oleomargarine	0.8916	8.09	0.30	4.02	1.46	4.24		62.19		No reaction.		1
2	" " " "	0.8638	9.68	0.17		1.43	4.68		63.52				2
3	Vermont " " "	0.8667	10.96	0.25	6.60	1.56	6.01		66.69				3
4	" " " "	0.8913	9.32	0.15	4.80	0.07			61.44				4
5	Woodlawn Dairy Co., "	0.8848	9.40	0.17	5.40	4.83		25.0°	62.83				5
6	" " " "	0.8911	9.86	0.20	6.80	0.48		25.5°	63.26				6
1	Oakdale M'f'g Co., "	0.8840	9.81	0.42	3.52	1.44	3.38	22.5°	60.62		No reaction.		7
2	Vermont " " "	0.8808	8.52	0.55	4.43	1.41	4.77	24.0°	59.11		Slightly dark.		8
3	Oakdale " " "	0.8835	8.53	0.42	5.17	1.36	5.95	23.0°	52.80	9.599	Purple brown.		9
4	" " " "	0.8865	10.69	0.27	2.99	1.21	2.96	25.0°	60.05		No reaction.	Highly color'd	10
5	" " " "	0.8834	7.37	0.35		1.16	5.29	24.5°	63.12		Purple brown.		11
6	" " " "	0.8906	8.00	0.35	3.75	2.59		25.0°	54.49	9.620	" "		12
7	" " " "	0.8914	6.86	0.42	3.42	1.77		22.5°	58.57		No reaction.	Highly color'd	13
8	Vermont " " "	0.8828	9.47	0.35	5.31	1.33	5.67	25.0°	66.50	9.795	Purple brown.		14
9	" " " "	0.8857	9.73	0.45	4.36	1.53	4.49	21.5°	68.03		No reaction.	Highly color'd	15
10	" " " "	0.8874	9.00	0.30	3.68	1.66	3.68	22.5°	66.59	9.649	Purple brown.		16
11	Woodlawn " " "	0.8992	9.23	0.35	3.97	1.47	3.78	22.0°	61.44		Slight dark'ng		17
	Swift & Co., "	0.8830	8.32	0.22	2.12	0.81	2.19	24.0°	60.67	9.644	No change.	Highly color'd	18
	Hammond, "	0.8891	9.15	0.22	6.69	1.43	6.21	25.0°	60.53	9.607	" "	V'y high'yc'l'd	19
	Brown, Fitzgerald & Co., "	0.8876	9.25	0.27	4.04	0.77	4.00	26.5°	53.37	9.574	" "		20
1	Woodlawn Dairy Co., "	0.8818	9.87	0.82	5.22	2.64	5.70	25.5°	58.12	9.613	" "		21
2	" " " "	0.8880	9.23	0.35	3.80	1.52	3.68	22.5°	61.80	9.670	No reaction.	Highly color'd	22
3	" " " "	0.8883	10.68	0.22	5.63	1.53	5.18	22.0°	65.73				23
4	" " " "	0.8943	7.91	0.22	3.17	1.13	3.24	23.0°	65.24				24
5	Goshen M'f'g Co., "	0.8998	9.37	0.22	5.82	1.63	5.42	23.5°	64.66	9.615	No reaction.		25
	Elgin Creamery, butter	0.8925	8.32	11.10	3.81	1.27	3.64	35.3°	37.75	9.327			26
	Plains, Va., "	0.8979	11.43	8.55	4.05	1.84	4.93	36.1°	36.86	9.362			27
	Armour & Co., best "	0.8984	12.98	10.82	4.04	1.30	3.94	33.5°	41.20	9.320			28
	" " " " oleomargarine								49.91	9.601	No reaction.		29
	" " " " cheap "								51.34	9.646	" "		30
	Elgin and ½ Woodlawn No. 2[8]								43.90	9.391			31
	½ " " ½ " " "								48.01	9.416			32
	½ " " ½ " " "								55.40	9.491			33
	Greensboro, N. C., sample[1]		7.81	8.52				37.5°	24.81				34

[1] Called butter.

exceedingly useful. The samples were forwarded to Prof. Atwater, prepared for combustion, without any description of their character being given except that they were fats. It is well understood that the estimation of the calories is of considerable use in a determination of the molecular weights of complex molecules and the results which we will report will serve to show, we think, practical application of the use of the bomb calorimeter.

This is best seen by a study of the following tables, which give in detail the examinations that are ordinarily made for oleomargarine and butter (Table I.), and accompanying these examinations the calories per gram. The samples were prepared for these latter determinations by washing, melting, filtering, and drying the samples at 100° C.

The figures given by different authorities for butter fat, vary slightly. Stohman gives the heat equivalent as determined by the potassium chlorate method as 9.192 small calories per gram, while by the oxygen method it was 9.231 calories per gram. The three samples of pure butter burned were from the following sources: No. 28, the best butter used by Armour & Co., in the manufacture of butterine. No. 26, was Elgin Creamery butter, and No. 27, obtained from a Virginia gentleman, who sent it as a sample of the best butter made on his place. Nos. 31, 32, and 33, were mixtures of Elgin butter and oleomargarine. The figures obtained for butter fat are a little higher than those Stohman gives for pure butter.

Table II. The steady increase in the calories of the mixtures is in proportion to the amount of oleomargarine added to the butter and this taken in conjunction with the iodine number gives additional confirmatory evidence of the character of the sample.

TABLE II.

MIXTURE COMPOSED OF DEFINITE PROPORTIONS OF ELGIN AND WOODLAWN No. 2^3.

Sample.	Actual iodine equivalent.	Theoretical iodine equivalent.	Actual combustion calories per gram.	Theoretical combustion calories per gram.
$\frac{3}{4}$ E and $\frac{1}{4}$ W, No. 2^3...	43.90	43.76	9.391	9.412
$\frac{1}{2}$ F and $\frac{1}{2}$ W, No. 2^3...	48.01	49.77	9.416	9.498
$\frac{1}{4}$ E and $\frac{3}{4}$ W, No. 2^3...	55.40	55.78	9.491	9.584

The theoretical calories per gram for the above mixtures as compared with those found are,

	Theory.	Found.
No. 31	9.412	9.391
No. 32	9.498	9.416
No. 33	9.584	9.491

The actual combustion of the sample containing a small admixture of oleomargarine falls a little lower than theory requires, but is sufficiently high to indicate at once that there is adulteration of the normal butter. The other two samples give results still more distinctive and characteristic. The determination of the calories would be sufficient, therefore, to detect oleomargarine. If not relied upon entirely it still furnishes very satisfactory evidence. One point to which attention should be called is the exceedingly low temperature at which the oleomargarines melted. They were purchased at the end of winter and probably made to suit the winter trade. If left in an open dish in the laboratory for a few hours they became soft and semi-fluid.

In the case of the lards from various sources the results are somewhat different and are not so distinctive as compared with compound lard, as the butter and oleomargarine. (Table III.) Still even here the determination of the calories taken in conjunction with other determinations, as the iodine absorption, will also be of use. Should the determination of the calories show a low figure one could conclude that the lard was either a compound or a lard from the caul, intestines, or head of the animals, while the determination of the iodine number and cotton-seed-oil test, would show at once whether the sample was a lard or a compound lard. The error of experiment in calorimetric work is usually counted at twenty-five calories per gram, but by careful work can be made less and a number of experiments in the same line as the above, would probably give data that would make the determination of the calories of still more practical value.

TABLE III.

ANALYSES OF SPECIMENS FROM ARMOUR & CO.

Quality.	Melting point.	Iodine equivalent.	Combustion calories per gram.	Cotton-seed oil, Bechi's test.
Lard, leaf.....	....	56.85	9.621	none.
" caul fat	40.0°	58.61	9.573	Slightly darken
" intestinal fat	40.7°	54.74	9.581	" "
" heads	29.5°	68.79	9.503	None.
" mixture of all fats...	....	63.86	9.654	"
" trimmings .	....	65.57	9.606	"
" compound, 1st grade.	....	86.18	9.583	Purple brown.
" compound, 2nd grade	....	86.57	9.530	" "
" shield	....	61.01	9.598	None.
" special pure	37.5°	63.63	9.617	"

In a recent number of this Journal, September, 1895, Wesson has very carefully reviewed the subject of the determination of the iodine absorption number in pure and compound lards, claiming that the figures heretofore given for pure lard were too low for the present methods of manufacture. This point also came up for incidental consideration in connection with our other examinations. We secured two sets of samples from Chicago, one sent direct from Armour & Co. (Table III), with the statement that the samples were what the names indicated. The other set of samples was accompanied by a certificate from the inspector testifying to the character of the material as forwarded.

TABLE IV.

ANALYSES OF LARDS FROM ARMOUR & CO.

Quality.	Iodine equivalent.	Cotton-seed oil, Bechi's test.
Leaf	55.60	No reaction.
Caul fat.....	58.08	" "
Intestinal fat.....	52.94	" "
Heads.....	62.36	" "
Trimmings	61.58	" "
Special pure.....	60.87	" "
Foreign shield.....	58.62	" "
Exp. Ref. Comp.....	69.79	Purple black.
Prime steam	65.97	No reaction.
Dom. comp.....	74.53	Purple black.

TABLE V.

Sample.	Iodine equivalent.	Cotton-seed-oil, Bechi's test.	Combustion calories per gram.
Lard No. 5	58.98	....	....
Lard Plains	50.49	....	9.606
Cottolene	90.89	Purple black.	....

In addition two other samples of lard, one from Virginia, the other from Rhode Island, were examined. The samples sent with the inspectors' certificate were freshly made, while the other set was older material. There is a decided variation in the iodine equivalent and in deciding upon the character of the lard, the origin of the sample should undoubtedly be taken into consideration. As this is often not possible a check upon the other results may be secured by the determination of the calories.

BIOCHEMIC LABORATORY, WASHINGTON, D. C.,
December 14th, 1895.

Discussion.—Mr. A. H. Sabin: I am very decidedly of the opinion that in investigations as to fats and oils, conclusive and satisfactory results can only be obtained by a comparison of methods. Such a method as this seems to me to be of a good deal of practical value because it is definite and positive. We make a combustion in this way and get some results which can be depended upon, and which can be verified; and the conditions are not difficult to duplicate. While I doubt if such a method will be of permanent value, because in such matters the ingenuity of the manufacturer is always pitted against the skill of the analyst, such a method always has weight, and must be taken in conjunction with other methods which also have weight and which also by themselves are not conclusive, but which have cumulative effect. I am certain that in regard to the vegetable fats it is only possible to arrive at just conclusions by a comparison of methods.